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**Legacy PBDEs and NBFRs in Sediments of the Tidal River Thames Using Liquid
Chromatography Coupled to a High Resolution Accurate Mass Orbitrap Mass Spectrometer**

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Abstract

Surface sediment samples (n=45) were collected along a 110 km transect of the river Thames in October 2011, starting from Teddington Lock out through the industrial area of London to the southern North Sea. Several legacy and novel brominated flame retardants (NBFRs) were analysed, including 13 polybrominated diphenyl ethers (PBDEs) (congeners 17, 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207 and 209), hexabromocyclododecane (HBCDDs), tetrabromobisphenol A (TBBPA), hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB or TBB), bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP or TBPH), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), anti/syn-dechlorane plus (a/s-DP), 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and α -, β -1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (α -, β -DBE-DBCH or TBECH). A novel analysis method based on liquid chromatographic separation, followed by high resolution accurate mass detection using the Orbitrap platform was used for quantification. Results revealed that BDE-209 had the highest concentrations (<0.1 to $540 \mu\text{g kg}^{-1} \text{ dw}$) and detection frequency, accounting for 95 % of all PBDE congeners measured. Indicative evidence of debromination of the PentaBDE technical mixture was observed through elevated relative abundance of BDE-28 in sediment compared to the Penta-BDE formulation. NBFRs were detected at comparable levels to PBDEs (excluding BDE-209), which indicates increasing use of the former. Spatial trend analysis showed that samples from industrial areas had significantly higher concentrations of $\Sigma_{12}\text{PBDEs}$, ΣHBCDDs , TBBPA, BEH-TEBP, BTBPE and TBP. Three locations showed high concentrations of HBCDDs with diastereomer patterns comparable to the technical mixture, which indicate recent input sources to the sediment.

Keywords: Brominated flame retardants, Spatial trends, Sources, Freshwater Environment

1 Introduction

In recent decades, a wide variety of brominated flame retardants (BFRs) have been added to consumer goods such as soft furnishings, building insulation foam, electronic and electrical goods. The most extensively used BFRs include: tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD) and three commercial mixtures of polybrominated diphenyl ethers (PBDEs); namely pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE) and decabromodiphenyl ether (DecaBDE)¹. Within the European Union, manufacture and new use of the PentaBDE and OctaBDE formulations were prohibited in 2004, and these formulations were listed under the UNEP Stockholm Convention on persistent organic pollutants (POPs) in 2009². Restrictions on the manufacture and use of DecaBDE have followed, and it was listed in 2017 under Annex A of the Stockholm Convention. A key consideration with respect to the listing of DecaBDE under the Stockholm Convention is its potential to form lower BDEs by various debromination processes³.

Due to legislative restrictions on manufacture and use of these BFRs, several so-called novel BFRs (NBFRs) are likely finding wider use⁴. In general, increasing levels of NBFRs are being detected in various matrices relevant to environmental and human health⁵. The environmental impact of NBFRs is potentially similar to the restricted BFRs⁶. Animal studies have shown that exposure to BFRs can have endocrine, reproductive, and behavioural effects at doses comparable to human exposure⁷. Human epidemiological studies have reported association between exposure to BFRs and adverse neurodevelopmental and reproductive effects in humans^{8 9 10 11}. Laboratory studies on NBFRs indicate genotoxicity in aquatic species¹², as well as cytotoxic and anti-proliferation effects with a possible induction of apoptosis in HepG2 cells¹³.

BFRs generally have limited biodegradability, are persistent and tend to accumulate in the environment¹⁴. Due to their chemical properties (i.e. low water solubility and high K_{ow} values), NBFRs tend to partition to organic carbon rich matter and have been detected in sediment, dust and sewage sludge around the world⁴. We therefore hypothesize that sediments represent important sinks for NBFRs. Studies on BFRs in sediments in the UK have been conducted on samples from lakes¹⁵⁻¹⁷, rivers and estuaries¹⁸⁻²¹, coastal^{19, 22} and marine regions^{19, 23}. However, apart from two UK studies^{19,24}, which analysed a broad range of halogenated flame retardants in both marine and fresh water sediments, other studies in the UK have focused mainly on PBDEs and HBCDDs. Given this lack of information on the levels and profiles of NBFRs in freshwater sediments, the aim of this study is to compare concentrations of 13 PBDEs, HBCDDs, TBBPA and 10 selected NBFRs in surficial sediments taken at 45 locations along the tidal reaches of the River Thames in the UK. In addition, we examine spatial variations in PBDE and NBFR concentrations relative to the location of putative source activities such as sewage outfalls, in an effort to identify potential sources of these BFRs to the river. The Thames was chosen as it is one of the major rivers in Europe, has fairly complex sediment transport dynamics owing to its high tidal range, morphology and geology²⁵. Its sediments are subject to regular capital and maintenance dredging which has the potential to mobilise and redistribute sediments or require disposal at sea or on-land. Recent evaluation of historical sediment profiles of mercury (Hg)²⁶ as well as surface distributions of phosphorus (P)²⁷ and natural tetraether lipids²⁸ confirm that contamination originates from both diffuse and point sources.

To the authors' knowledge, this is the most extensive comparison yet of levels, spatial trends, and potential sources of PBDEs and NBFRs in river sediments. Moreover, our study

exploits the potential of high resolution Orbitrap mass spectrometry for multi-residue analysis of a broad range of BFRs and NBFRs in a single run with sensitive, rapid and reliable measurement of target analytes, as well as their potential degradation products.

2 Materials and Methods

2.1 Study area

The River Thames is one of the major rivers in Europe, with a total length of 354 km, a catchment area of 12,935 km² and an average discharge of 65.8 m³/s. It has a spring tidal range of between 5.2–6.6 m and extends 110 km from Teddington Lock through London and out to the southern North Sea (Figure 1). The Thames basin contains many major urban centres accommodating around a fifth of the UK population (ca. 12 million) of which > 10 million live in Metropolitan London. London is intersected by 33 tributaries and about 60 municipal and commercial discharge points. Numerous industries, ports, sewage treatment plants and power stations discharge into the tidal Thames²⁸.

2.2 Sample collection

Sampling of sediments from the River Thames was carried out in October 2011 at the locations shown in Figure 1. All sites were accessed via a jet boat using predetermined GPS coordinates to accurately locate each position to ± 3 m^{26, 28}. At each location, surface sediments (0-5 cm) were collected from four corners of a square of ca. 2 m² area, using either a stainless steel trowel or a polycarbonate tube fitted with a core catcher manually driven into the surface²⁹. The four corner samples and one central sample were combined and transported to shore in a polyethylene zip lock bag. Sediments were immediately frozen at -18 °C in the dark to avoid post collection chemical changes and physical movement, then

transported frozen to the laboratory within 3 days. Each sample was freeze-dried, sieved to pass a 2 mm brass mesh and ground to a fine powder using an agate ball-mill and stored in sealed polyethylene bags in a desiccator in the dark³⁰.

2.3 Study area

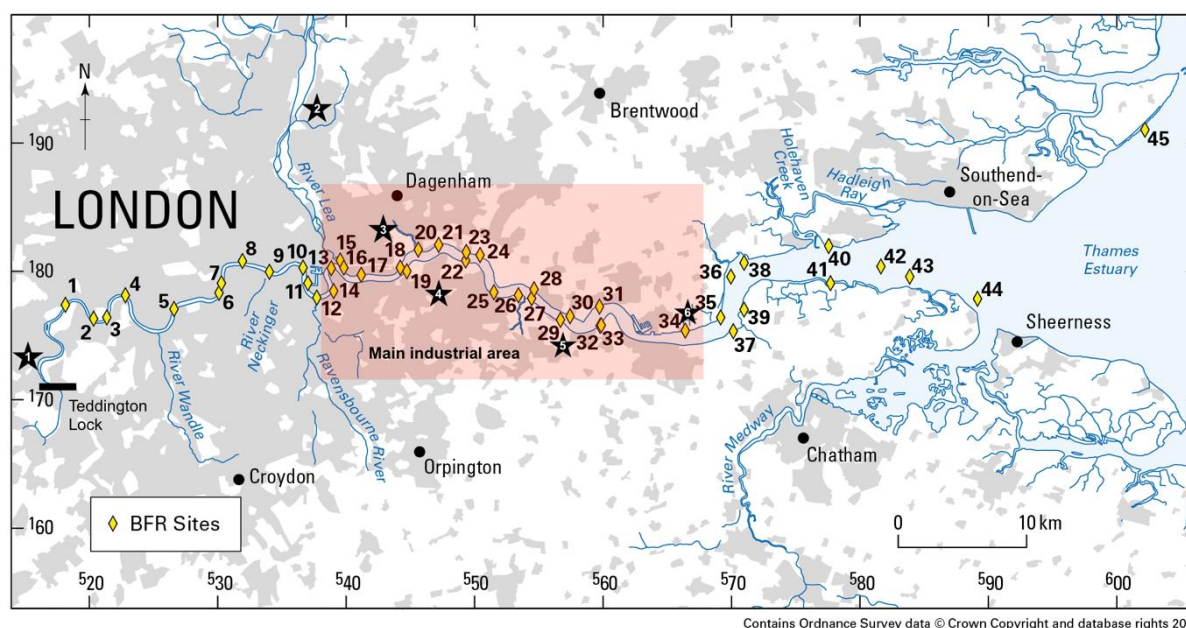


Figure 1. Sampling locations (yellow diamonds) of surface sediments along the Thames Estuary. Stars represent the main discharge locations of sewage effluents; 1. Mogden; 2. Abbey Mills; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP; 6. Tilbury STP. Red shaded area shows the main industrial discharge area on the Thames (samples 13-34). The Teddington Lock on the left divides the river Thames into tidal and non-tidal sections. Adapted from Lopes dos Santos and Vane²⁸. STP – sewage treatment plants

2.4 Chemicals and Standards

All solvents used were purchased from Fisher Scientific (Loughborough, UK) and were of HPLC grade or higher. Native and labelled high purity standards for PBDEs (BDE-17, BDE-28, ¹³C-BDE28, BDE-47, BDE-77, BDE-99, BDE-100, ¹³C-BDE100, BDE-128, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207, BDE-209 and ¹³C-BDE209), hexabromobenzene (HBB), 2,4,6-tribromophenol (TBP), α,β and γ-HBCDDs / ¹³C-α,β-, and

γ -HBCDDs, TBBPA / ^{13}C -TBBPA and NBFs 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), ^{13}C -EH-TBB, bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), ^{13}C -BEH-TEBP, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), ^{13}C -BTBPE, decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), anti/syn-dechlorane plus (a/s-DP), 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and α,β -1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α,β -DBE-DBCH) were all purchased individually from Wellington Laboratories Inc. (Guelph, Canada) and mixed as required. Internal standards were used for the quantification of several native compounds as listed in Table SI 4. Florisil HyperSep™ SPE cartridges (1 g, 60 cc), concentrated sulfuric acid, copper powder (particle size <100 μm) and anhydrous sodium sulfate (dried overnight at 120 °C) were acquired from Thermo Fisher Scientific (Loughborough, UK). The standard reference material (SRM 1944, "New York/New Jersey Waterway Sediment" certified for PCBs, PAHs and PBDEs) was obtained from the National Institute of Standards and Technology - NIST (Gaithersburg, MD, USA).

2.5 Sample extraction/clean-up

2 g of freeze-dried sediment were weighed into a pre-cleaned glass extraction tube and spiked with 20 μL of the internal standard mixture (^{13}C -BDE-28, BDE-77, BDE-128, ^{13}C -BDE-209, ^{13}C -TBBPA, ^{13}C - α,β -, and γ -HBCDDs, ^{13}C -EH-TBB, ^{13}C -BEH-TEBP and ^{13}C -BTBPE), along with 2 g of copper for sulfur removal. Samples were then extracted using 4 mL of hexane:acetone (3:1 v/v), vortexing for 5 min, followed by ultrasonication (20 min) and centrifugation (5 min at 4000 rpm). This procedure was repeated twice. The combined extract was then evaporated to dryness under a gentle stream of N_2 and reconstituted in 2 mL of hexane. This was followed by a sulfuric acid wash of the extract, with the layers allowed to separate overnight. The organic phase was collected and the acid layer washed

twice with 2 mL of hexane. The combined extracts were then reduced to ~1 mL under a gentle stream of N₂ and loaded onto a conditioned HyperSep™ 1 g Florisil SPE cartridge, on top of which 1 g of sodium sulfate was added. Subsequent elution was performed with 20 mL of hexane:dichloromethane (1:1 v/v), with TBBPA eluted in a second fraction with 15 mL of methanol. Both fractions were combined, concentrated to dryness under a N₂ flow in a Turbovap and reconstituted in methanol:toluene (1:1 v/v) containing 200 pg µL⁻¹ of ¹³C-BDE-100 as a recovery determination standard.

2.6 Instrumental analysis

2 µL of each sample were analysed on a UPLC-Orbitrap-HRMS instrument (Thermo Fisher Scientific, Bremen, Germany) composed of an UltiMate® 3000 high performance liquid chromatography system equipped with a HPG-3400RS dual pump, a TCC-3000 column oven and a WPS-3000 auto sampler coupled to a Q-Exactive™ Plus Orbitrap mass spectrometer. Chromatographic separation was performed on a Thermo Scientific Accucore™ RP-MS column (100 x 2.1 mm, 2.6 µm) with water (mobile phase A) and methanol (mobile phase B). A gradient elution programme at a flow rate of 400-500 µL min⁻¹ was applied as shown in Table SI 2 for a total run time of 17 min.

All parent BFRs were determined in negative atmospheric pressure chemical ionization (APCI) mode. The parameters of the Orbitrap were set as follows: (-) APCI full scan mode at 70000 FWHM (full width at half maximum at 200 m/z and scan rate of 3 Hz at 200 m/z), AGC target 1e⁶, maximum injection time 100 ms, scan range 250 to 1000 m/z, profile spectrum data type, sheath gas (nitrogen) flow rate 25 AU (arbitrary units), aux gas (nitrogen) flow rate 5 AU, discharge current 30 µA, capillary temperature 250 °C, S-lens RF level 50 AU and aux gas heater temperature 320 °C. For screening identification of possible more polar

degradation products and confirmation purposes, sediment extracts were also analyzed using the more universal, softer electrospray ionisation (ESI) in negative mode, as described in the Supporting Information section. Both the HPLC gradient programme and ionisation values were optimized based on the measurement of reference standard solutions. Screening for brominated compounds was conducted using an All Ion Fragmentation Scan (AIF) in parallel to the Full Scan measurement and by monitoring the bromine mass trace in the final data raw files as an indicator for the presence of brominated compounds. Subsequent identification of specific compounds was based on exact mass (Table SI-4) and isotopic pattern. Trace Finder™ version 3.3 software (Thermo Fisher Scientific, Bremen, Germany) was used to process raw data files, while quantification of the compounds of interest was conducted using Microsoft Excel 2010.

2.7 QA/QC

The standard reference material SRM 1944 (NIST) for sediment was used to evaluate the accuracy of the method for PBDEs and HBCDDs. One SRM sample was analysed for every 15 sediment samples. Values obtained for the SRM 1944 were generally in good accordance with the certified levels (Table SI 3). In addition, non-certified compounds including BTBPE, BEH-TEBP, PBEB, TBP, BB153 and DP were detected in the SRM 1944, although concentrations varied between replicates (9-65% RSD, Table SI 3).

Recoveries for internal standards were in the range of 90 to 120 % for all samples, except for ¹³C-TBBPA, where recovery values were around 50 %, with detailed information in Table SI 4.

Limits of detection (LOD) and limits of quantification (LOQ) were estimated based on method described by Taylor³¹ (Table SI 4). In brief, standards were analysed in replicates

(n=10). The standard deviation of each measured concentration was plotted versus the specified concentration, giving a y-axis intercept of the resulting regression line corresponds to s_0 . The LOD is then defined as $3 \times s_0$, while the LOQ is defined as $10 \times s_0$. LODs in sediment matrix in general ranged from 0.0001 $\mu\text{g/kg}$ (for HBCDDs) to 1.1 $\mu\text{g/kg}$ (for DBE-DBCH), with values for BDEs ranging from 0.001 $\mu\text{g/kg}$ (for BDE-209) to 0.37 $\mu\text{g/kg}$ (for BDE-17). To minimise blank contamination, all glassware was cleaned by soaking in a detergent solution overnight, before rinsing with deionised water. This was followed by washing with acetone, hexane, toluene and dichloromethane and subsequent baking at 120 °C overnight. One method blank (sodium sulfate replacing the sediment) was analyzed with every set of 6 samples. For some legacy BFRs (BDE-100, BDE-153, BDE-183, BDE-209 and HBCDDs) concentrations in blanks were detected just above LODs up to $2.5 \pm 1.2 \text{ pg g}^{-1} \text{ dw}$ for BDE-209. For NBFRs, only TBP and TBBPA were detected in blanks at average concentrations of $106.2 \pm 30 \text{ pg g}^{-1} \text{ dw}$ and $186.2 \pm 43 \text{ pg g}^{-1} \text{ dw}$ respectively. Target analytes of the associated batch were blank corrected by subtraction of average blank concentrations. Concentrations in samples were therefore blank corrected by subtraction of average blank concentrations.

2.8 Statistical analysis

Statistical analysis of the data was performed using IBM SPSS statistics software version 23. A one-way ANOVA was used for testing significant differences between arithmetic means. For statistical purposes, “non-detect” values were replaced with zero, while “detect” values with a concentration below the LOQ were assigned a value of the LOQ/2 or in cases of a detection frequency below 50% the LOQ was multiplied by the detection frequency factor. P values < 0.05 were taken to indicate statistical significance.

3 Results and Discussion

3.1 Levels and trends of PBDEs and NBFRs in sediments

Mean, median and concentration ranges of our target BFRs in surface sediments from the River Thames are summarised in Table 1, while concentrations of individual PBDE congeners are provided in Table SI 6. While individual HBCDD diastereomers were measured, they are reported in Table 1 as Σ HBCDD only. By comparison, *anti*- and *syn*-DP as well as α - and β -DBE-DBCH were reported as Σ DPs and Σ DBE-DBCH respectively owing to our inability to chromatographically resolve the individual isomers. To account for potential variability of concentrations due to organic carbon content, organic carbon normalisation was conducted on all sample concentrations using the measured total organic carbon (TOC) for each sample, as described in the supporting information. No correlation between BFR concentrations and TOC values was observed in the studied samples. This is likely explained by the fact that samples were taken from different locations with diverse source input strengths. If samples originate from the same location (such as sediment cores) with the same source input strength, a positive linear correlation between TOC and BFR dry weight concentration would be expected. Similarly, for the composition of the sediment, no correlation between the BFR concentration and its geological composition (clay, silt or sand content) was observed in this study.

254 **Table 1. Summary of the concentrations in both $\mu\text{g kg}^{-1}$ dry weight and $\mu\text{g kg}^{-1}$ organic carbon of selected BFRs in surficial sediments from the**
255 **River Thames**

Compound	DF (%)	Median	Average	Range	Median	Average	Range
		$\mu\text{g kg}^{-1}$ dry weight			$\mu\text{g kg}^{-1}$ organic carbon		
$\Sigma_{12}\text{BDEs}$	16-100	3.8	5.9	n.d. – 29	182	228	n.d. – 672
BDE-28	27	<0.2	0.4	<0.2 – 4.0	n.d.	12	n.d. – 116
BDE-47	53	<0.03	0.2	<0.03 – 2.5	n.d.	6.7	n.d. – 48
BDE-99	71	0.5	0.8	<0.05 – 4.4	15	28	n.d. – 130
BDE-153	16	<0.01	0.03	<0.01 – 0.6	n.d.	1.2	n.d. – 33
BDE-183	71	0.05	0.1	<0.01 – 0.7	0.4	3.3	n.d. – 23
BDE-206	96	2.6	3.3	<0.1 – 11.7	115	135	n.d. – 389
BDE-209	100	148	174	0.03 - 535	6969	7673	0.03 - 20762
ΣHBCDD	91	1.9	3.7	<0.001 – 38	67	157	n.d. – 1357
TBBPA	98	0.6	0.6	<0.02 – 2.6	21	34	n.d. – 476
EH-TBB	0	<0.03			<0.03		
BEH-TEBP	76	2.1	3.5	<0.02 – 14	100	134	n.d. – 445
BTBPE	51	<0.02	0.4	<0.02 – 3.8	0.7	15	n.d. – 142
TBP	69	0.1	0.1	<0.01 – 0.4	3.5	4.6	n.d. – 34
anti-/syn-DP	11	<0.04	2.0	<0.04– 66	n.d.	51	n.d. – 1249
PBEB	7	<0.06	1.7	<0.06 – 48	n.d.	53	n.d. – 1385
DBDPE	20	<0.45	1.3	<0.45 – 24	n.d.	42	n.d. – 1154
α/β-DBE-DBCH	0	<1.1			n.d.		
HBB	0	<0.03			n.d.		
BB153	0	<0.01			n.d.		

256 * $\Sigma_{12}\text{BDEs}$ does not include BDE-209

257 * n.d. - not detected – NB for organic carbon normalised data, detection limit differs for each sample due to varying TOC content

258 * DF (%) – detection frequency

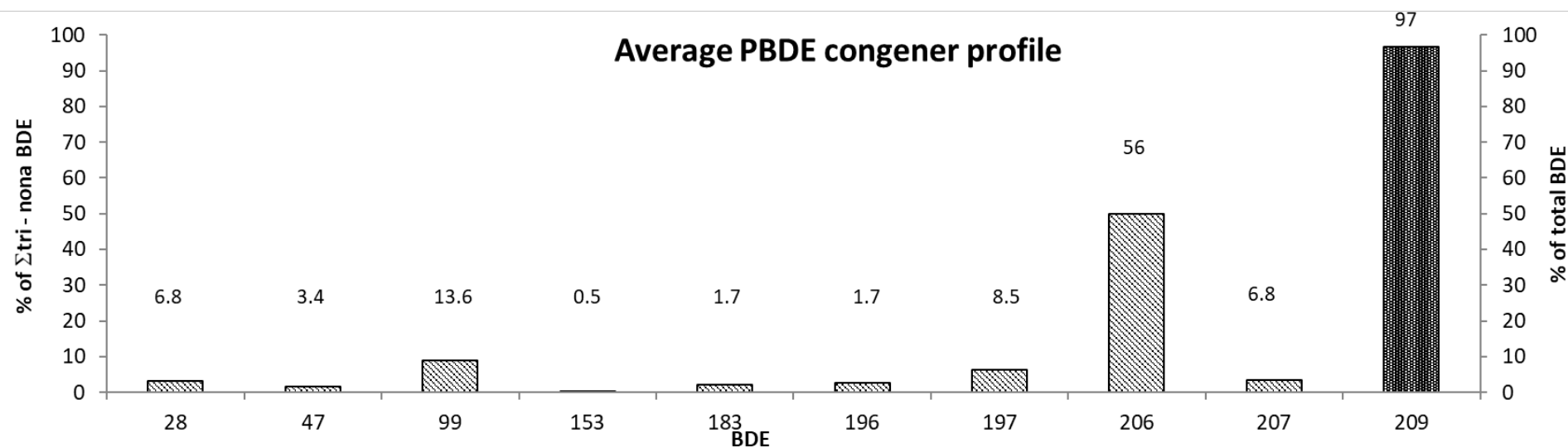
259 * < indicates the value of the LOD

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265 **Figure 2. Average PBDE congener profile in all sediment samples, expressed as % Σ tri-nona-BDEs. BDE-209 is on a different scale, expressed as**
266 **% Σ BDEs. Average percent contributions are indicated above each congener.**

3.2 PBDEs

PBDE concentrations varied widely along the River Thames transect BDE-209 was the predominant congener in all sediments, accounting for on average 96.7 % of total PBDEs detected (Figure 2). This is in agreement with other studies, for example Vane *et al.*, who reported BDE-209 to represent 80 % of total PBDEs in sediments collected from the Clyde Estuary around Glasgow, UK³². This indicates a higher proportion of the DecaBDE formulation in our samples, further supported by high concentrations of BDE-206. Similarly, other studies reported nona-brominated PBDE congeners as the second most abundant after BDE-209 in river sediment samples of the UK (inner Clyde estuary)³² and China (industrial area of the Dongjiang river)³³, possibly indicating degradation of BDE-209 to form lower brominated congeners. A comparison of our data to the technical Deca-BDE formulation follows later.

Concentrations of BDE-209 ranged from <0.1 to 540 $\mu\text{g kg}^{-1}$ dw (<0.1 to 20762 $\mu\text{g kg}^{-1}$ OC). Other PBDEs were detected at lower concentrations, with prominent congeners being BDE-206, followed by BDE-99 and BDE-28. Sediments from several UK lakes³⁴ contained BDE-209 at concentrations ranging from 1.63 to 116 $\mu\text{g kg}^{-1}$ dw. Meanwhile, river and marine sediments from various locations around the UK¹⁹ were reported between 0.3 – 1333 $\mu\text{g kg}^{-1}$ dw, 1 – 2337 $\mu\text{g kg}^{-1}$ dw for sediments of the river Clyde³² and 2 – 98125 $\mu\text{g kg}^{-1}$ dw for Scottish sediment cores³⁵. This sets our study at the lower end of previously detected concentrations of BDE-209 in UK sediments.

Harrad recently reviewed the concentrations of legacy BFRs in UK environmental samples³⁶. Where BFR levels in UK river and lake sediments were reported, BDE-209 was the prevailing congener, followed by BDE-99 and BDE-47. Interestingly in our study, levels for BDE-28 were

higher than those found for BDE-47, suggesting a potential degradation of higher molecular weight congeners to form BDE-28.

A recent study determined concentrations of PBDEs in sediments from the Thames estuary, reporting a concentration range for Σ_6 BDEs (congeners 28, 47, 99, 100, 153 and 154) of <MDL to $14.4 \mu\text{g kg}^{-1} \text{ dw}^{21}$. This is in good accordance with our results, that reported concentrations for the same congeners ranging from n.d. to $12.8 \mu\text{g kg}^{-1} \text{ dw}$. Barber *et al.* reported concentrations of Σ_{11} BDEs (i.e. excluding BDE-209) to fall between n.d. and $32.2 \mu\text{g kg}^{-1} \text{ dw}$ in river and marine sediments around the UK¹⁹, which is comparable to our range of Σ_{12} BDEs of n.d. to $29 \mu\text{g kg}^{-1} \text{ dw}$.

3.3 HBCDDs and TBBPA

HBCDDs (sum of α -, β -, and γ HBCDD) were detected in most samples (91 % detection frequency) at an average concentration of $3.7 \mu\text{g kg}^{-1} \text{ dw}$, which is comparable to our average concentration of Σ_{12} BDEs (excluding BDE-209) of $5.9 \mu\text{g kg}^{-1} \text{ dw}$. Concentrations of Σ HBCDDs ranged from n.d. to $38 \mu\text{g kg}^{-1} \text{ dw}$. A study on estuarine and marine sediments around the UK reported a comparable range from <MDL to $47.2 \mu\text{g kg}^{-1} \text{ dw}^{19}$. Values for lake sediments in the UK ranged from 0.42 to $7.9 \mu\text{g kg}^{-1} \text{ dw}^{34}$. Higher values were detected in the River Skerne in northeast England with concentrations from <2.4 up to $1680 \mu\text{g kg}^{-1} \text{ dw}^{20}$, likely originating from the vicinity of a former BFR manufacturing site. HBCDD concentrations in a study of coastal marine sediments were lower with maximum values up to 1.6 and $1.8 \mu\text{g kg}^{-1} \text{ dw}$ reported for southern and northern UK respectively²⁴.

TBBPA was found in all but one Thames sediment, with a maximum concentration of 2.6 $\mu\text{g kg}^{-1}$ dw and an average of 0.6 $\mu\text{g kg}^{-1}$ dw, in which is an order of magnitude lower than found in this study for HBCDDs and Σ_{12} BDEs. Comparatively few studies have reported TBBPA concentrations in European sediment samples. Sediments from the southern and northern UK coast were reported to contain up to 6.4 $\mu\text{g kg}^{-1}$ dw for TBBPA and an average of 1.7 and 2.7 $\mu\text{g kg}^{-1}$ dw respectively²⁴. Interestingly however, TBBPA was the predominant compound with a detection frequency of 87 % in these coastal sediments. Morris *et al.*²⁰ analysed riverine and estuarine sediments from various rivers in the UK and found high average values of 451 $\mu\text{g kg}^{-1}$ dw and up to 9750 $\mu\text{g kg}^{-1}$ dw in the River Skerne. These elevated concentrations were attributed to the vicinity of sampling sites to a former BFR manufacturing site. TBBPA levels detected in our study are more comparable to those reported in sediment samples from rivers in The Netherlands and Germany with average values of 2.2 $\mu\text{g kg}^{-1}$ dw²⁰ and 0.3 $\mu\text{g kg}^{-1}$ dw²⁴ respectively.

3.4 NBFRs

One or more NBFRs were quantified in most samples at varying concentrations (Table 1) in the following order (detection frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %), with DBDPE (20 %), DP (11 %) and PBEB (7 %) identified in fewer samples. Where detected, concentrations of NBFRs were comparable to those of PBDEs (excluding BDE-209). Target compounds like EH-TBB, HBB, BB-153 and α/β -DBE-DBCH were not detected in any of the studied samples.

Consistent with our study, Barber *et al.*¹⁹ did not detect HBB, BB-153 and DBE-DBCH in 42 marine and river sediments samples from around the UK, while EH-TBB was detected in only one sample at a concentration of 0.29 $\mu\text{g kg}^{-1}$ dw. In addition, EH-TBB has been reported in

337 sediment samples from UK lakes³⁴ and southern and northern coastal locations, with
338 maximum concentrations of 1.35 $\mu\text{g kg}^{-1}$ dw and 26 % relative contribution in the
339 investigated area²⁴.

340 To our knowledge, this is the first study to detect BEH-TEBP in UK sediments (Table 1),
341 although this FR has already been reported in sediments from South Africa^{37, 38} and China^{39,}
342 ⁴⁰. We detected BEH-TEBP in 76 % of our samples with an average of 3.3 $\mu\text{g kg}^{-1}$ dw (134
343 $\mu\text{g kg}^{-1}$ OC) and maximum values of up to 14 $\mu\text{g kg}^{-1}$ dw (445 $\mu\text{g kg}^{-1}$ OC). This finding is
344 comparable to values of La Guardia *et al.* in South Africa (average of 96 ng g⁻¹ OC, 60 %
345 detection rate) and Zhu *et al.* in China (average of 1.01 ng g⁻¹ dw).

346 BEH-TEBP and EH-TBB are two of the main constituents of the technical flame retardant
347 mixture Firemaster 550 (FM-550). In the present study, interestingly only BEH-TEBP was
348 detected, possibly reflecting the infrequent use of FM-550 in the UK. The relative abundance
349 of these two NBFRs in the Thames estuary may thus be explained by applications other than
350 FM-550. For example, BEH-TEBP is also used as a plasticiser, in contrast to EH-TBB for which
351 the main application is as a flame retardant⁴¹ and thus might explain our findings. Several
352 studies in the UK have targeted both EH-TBB and BEH-TEBP in the indoor and outdoor
353 environment. These studies focused on indoor dust⁴², indoor⁴³ and outdoor air⁴⁴, food and
354 human milk⁴⁵, as well as soil samples⁴⁴. In general, where reported, BEH-TEBP was detected
355 at concentrations 1-2 orders of magnitude higher than what was found for EH-TBB.

356 Furthermore, EH-TBB was not detected in UK outdoor air or soil⁴⁴, consistent with its
357 absence here in Thames sediments.

358 Concentrations of BTBPE in our sediments reached up to 3.8 $\mu\text{g kg}^{-1}$ dw with a detection
359 frequency of 51 %, which accords well with Barber *et al.*¹⁹ who reported a maximum of 1.8

360 $\mu\text{g kg}^{-1}$ dw and a detection frequency of 48 %. The presence of BTBPE was also reported in
361 lake sediment in the UK³⁴.

362 TBP was detected in 69 % of our sediments at relatively low concentrations up to $0.4 \mu\text{g kg}^{-1}$
363 dw. To our best knowledge, TBP has not been reported in UK sediments so far. DBDPE, DP
364 and PBEB in our study were only detected in a small number of samples. DBDPE has been
365 reported in sediments throughout Europe, including lake sediments in the UK (up to $6.4 \mu\text{g}$
366 kg^{-1} TOC)³⁴ and Italy (up to $280 \mu\text{g kg}^{-1}$ dw)⁴⁶, as well as river sediments in the Netherlands⁴⁷
367 and Spain (both up to $24 \mu\text{g kg}^{-1}$ dw)⁴⁸. PBEB has been reported both in UK and German
368 sediments^{19, 24}, while the same goes for DP^{24, 49}. HBB and BB-153 were not detected in this
369 study, but their presence has been previously reported in surface and tributary sediments of
370 Lake Ontario⁵⁰, with HBB also detected in river sediments in Germany²⁴. An extensive review
371 on the presence of emerging brominated flame retardants in sediments around the world
372 can be found elsewhere⁵¹.

373 The absence of DBE-DBCH from our sediments is perhaps surprising as DBE-DBCH has been
374 reported to be the predominant NBFR in UK indoor air and dust⁴³, outdoor air⁴⁴, as well as
375 UK human milk and diet samples⁴⁵. This may be attributable to the physico-chemical
376 properties of DBE-DBCH, namely its relatively high volatility and low K_{ow} compared to lower
377 brominated BDEs. This is likely to minimise its partitioning to sediment. Benthic degradation
378 processes are a further possible cause and have been reported for DBE-DBCH in aerobic and
379 anaerobic soil⁵². In European sediment it has been reported in German river sediments²⁴.
380 Outside Europe, DBE-DBCH was reported in sediments of the Great Lakes⁵³ for the first time
381 in 2012, as well as in Chinese river and marine sediments^{39 40}.

3.5 Spatial trends in concentrations of PBDEs and NBFRs

Spatial variation in BFR concentrations in sediments from the River Thames is shown in Figure 3 for Σ_{12} BDEs, HBCDDs and TBBPA (top), as well as Σ_{12} BDEs, BEH-TEBP, BTBPE and TBP (bottom). As shown, samples from the industrial area showed higher concentrations compared to both: (a) samples from the upper and (b) outer Thames. Inspection of the lower panel in Figure 3 reveals that concentrations of Σ_{12} BDEs and BEH-TEBP show a similar concentration pattern along the river, possibly indicating the same source input. BTBPE and TBP on the other hand show only a few localised input hotspots.

HBCDDs in the industrial area showed three distinct locations with elevated concentrations compared to the median concentration of 1.9 $\mu\text{g/kg dw}$, around Gallions Reach (site nr. 18, 38 $\mu\text{g/kg dw}$), St Clement's Reach (nr. 31, 23 $\mu\text{g/kg dw}$) and Tilbury (nr. 34, 7.9 $\mu\text{g/kg dw}$). A possible explanation could be the vicinity to sewage discharge locations, in close vicinity to Abbey Mills STP (site 18), Long Reach STP (site 31), and Tilbury STP (site 34). Other sources impacting the sediments in this area could be discharges from activities utilising HBCDDs in their products, such as building and construction facilities, as well as textile manufacturers. Inspection of HBCDD diastereomer profiles at the three locations above, revealed the profile to resemble that of the technical mixture, with γ -HBCDD predominant (85-92 %), followed by α -HBCDD (6-12 %) and β -HBCDD (2-3 %) only present in small quantities (Figure 4). This could indicate fresh input sources at the locations of the analysed sediments, as the diastereomer profile in these samples differs markedly from that in other samples (Figure 5). On average, the diastereomer profile in samples from the industrial area contained mainly γ -HBCDD, followed by α -HBCDD and only minor amounts of β -HBCDD, while in the non-industrial area the ratio between the three stereoisomers was more equal (Figure 5).

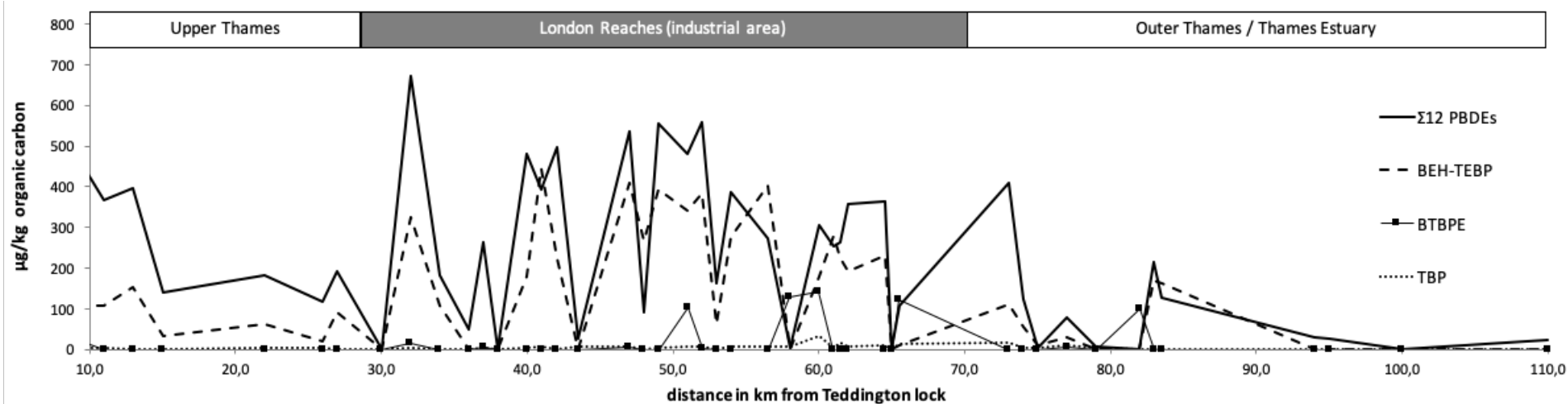
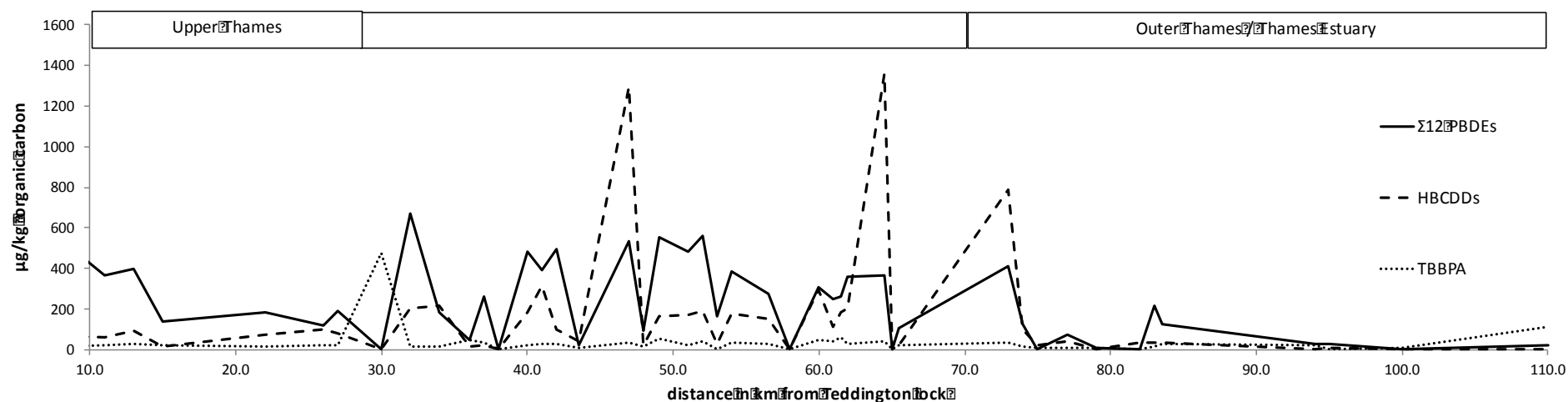
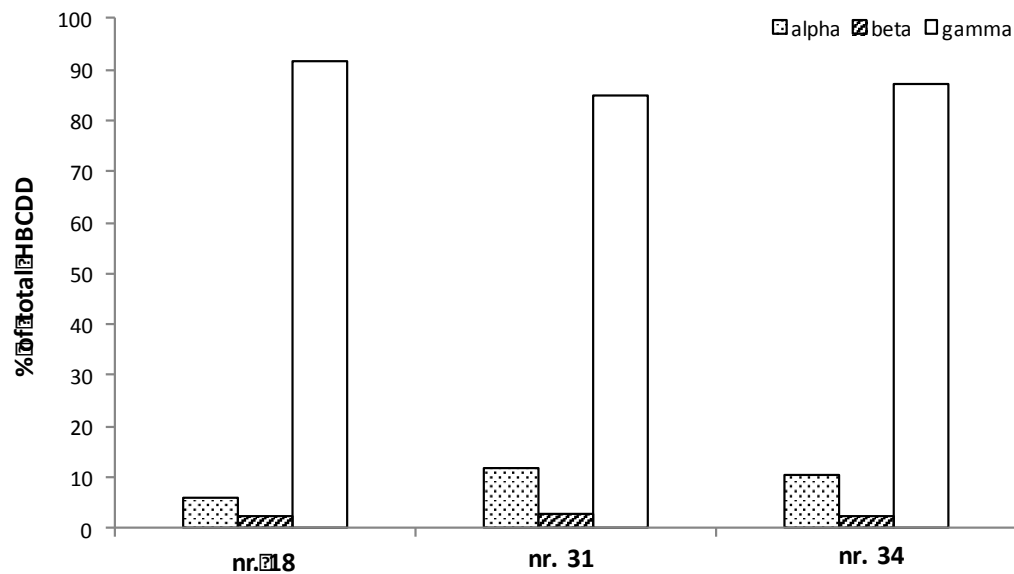


Figure 3. Spatial trends for Σ_{12} BDEs, HBCDDs, and TBBPA (top) and Σ_{12} BDEs, BEH-TEBP, BTBPE, and TBP (bottom) measured (in $\mu\text{g kg}^{-1}$ organic carbon) along the river Thames, with an approximate distance (km) from Teddington Lock.

412

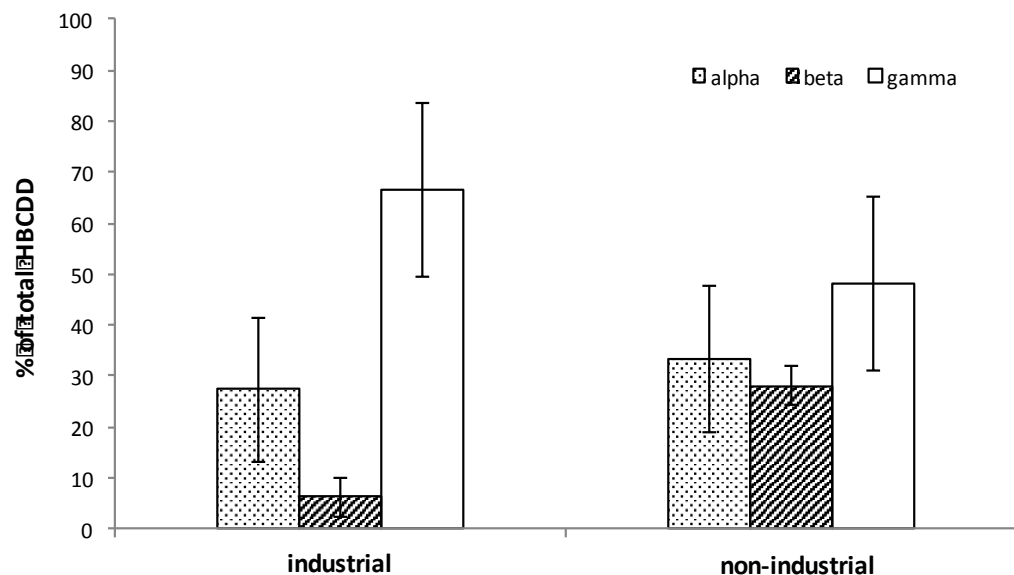


413

414 **Figure 4. HBCDD diastereomer profile in sediment from location #s 18, 31, and 34**

415

416



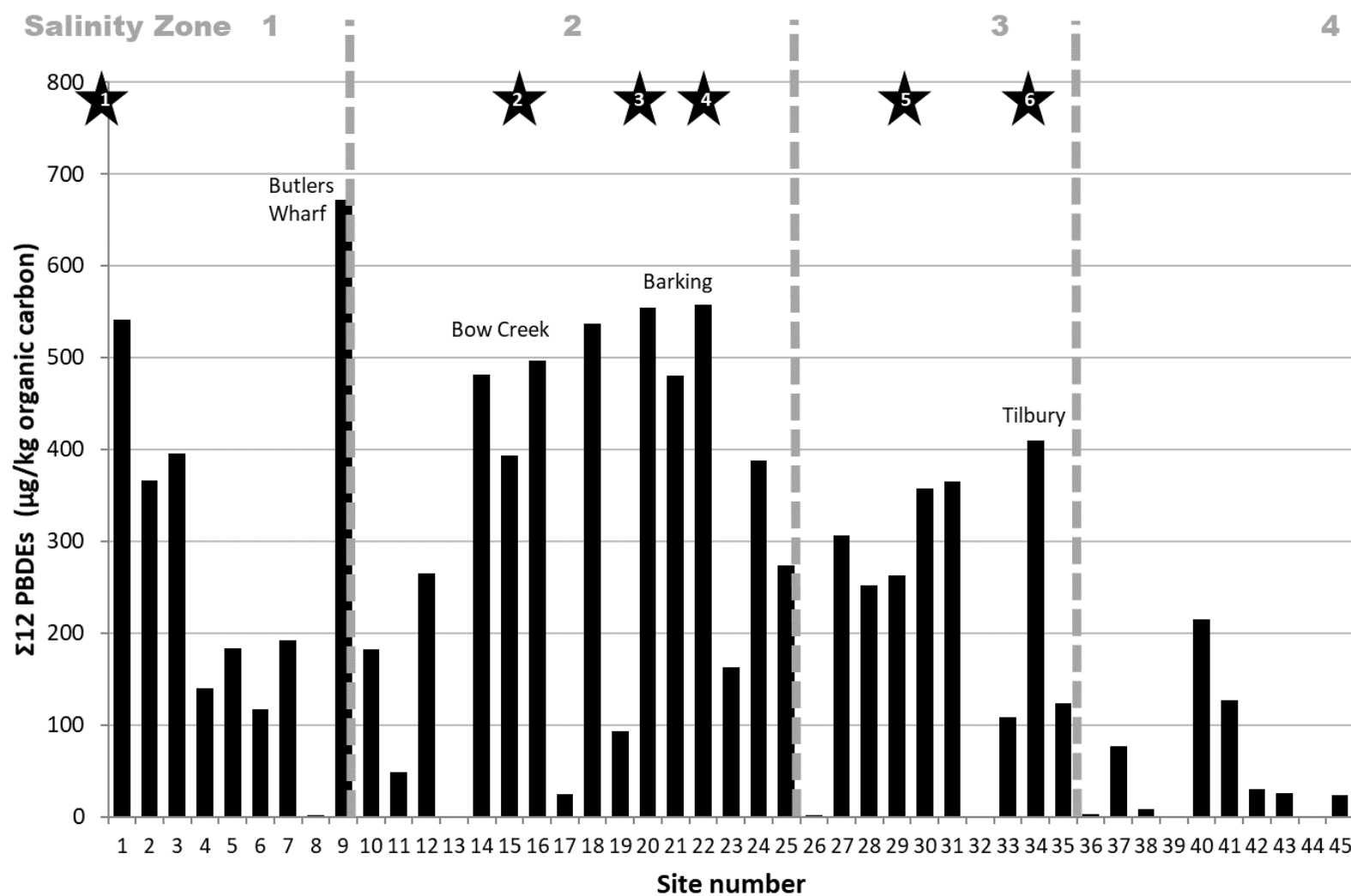
417

418 **Figure 5. Average HBCDD diastereomer profile in industrial and non-industrial area**

419

420 Figure 6 and Figure 7 illustrate the spatial variation in organic carbon-normalised
 421 concentrations of Σ_{12} BDEs and BDE-209 respectively. There is a general high-high-medium-
 422 low concentration profile from west to east for Σ_{12} BDEs (with average concentration values

423 for the 4 zones of 290, 309, 219 and 51 $\mu\text{g kg}^{-1}$ OC), while for BDE-209 we observe a
424 medium-high-high-low profile (7291, 9299, 9834 and 3255 $\mu\text{g kg}^{-1}$ OC), and a less marked
425 attenuation in concentrations on travelling west to east. This – coupled with an ANOVA test
426 that showed significantly ($p<0.05$) higher SPBDE concentrations in the industrial area but no
427 such spatial difference for BDE-209 - could be a possible indication for different sources of
428 the two groups of compounds. The general decline from west to east for $\Sigma_{12}\text{BDEs}$ is probably
429 driven by increasing distance from London and associated urban sources, as well as
430 flocculation-deposition of sediment controlled by salinity (salting-out) with increasing
431 proximity to the coast. The four salinity zones indicated were adapted from the study of
432 Pope *et al.*⁵⁴. The observed variability in the PBDE transect data can be explained by the fact
433 that suspended particles can travel up and down-stream by 10 - 20 km on one tide.



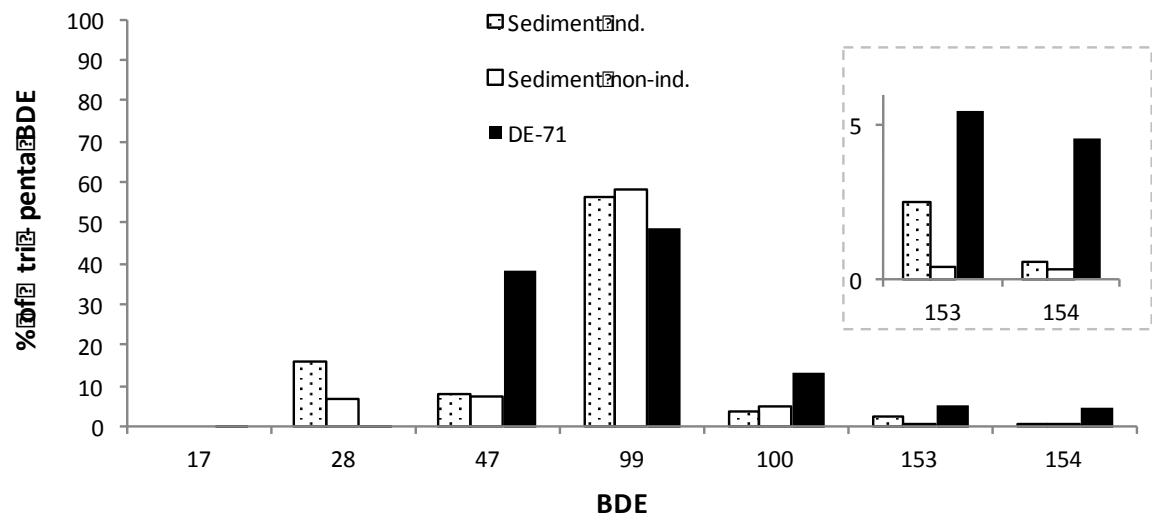
434

435 **Figure 6. Concentrations ($\mu\text{g kg}^{-1}$ organic carbon) of Σ_{12} PBDEs in River Thames sediments at each sampling location. Stars represent the main**
 436 **discharge locations of sewage treatment plants (STPs); 1. Mogden STP; 2. Abbey Mills STP; 3. Beckton STP; 4. Crossness STP; 5. Long Reach STP;**
 437 **6. Tilbury STP. Adapted from Lopes dos Santos and Vane²⁸**

3.6 PBDE/NBFR patterns

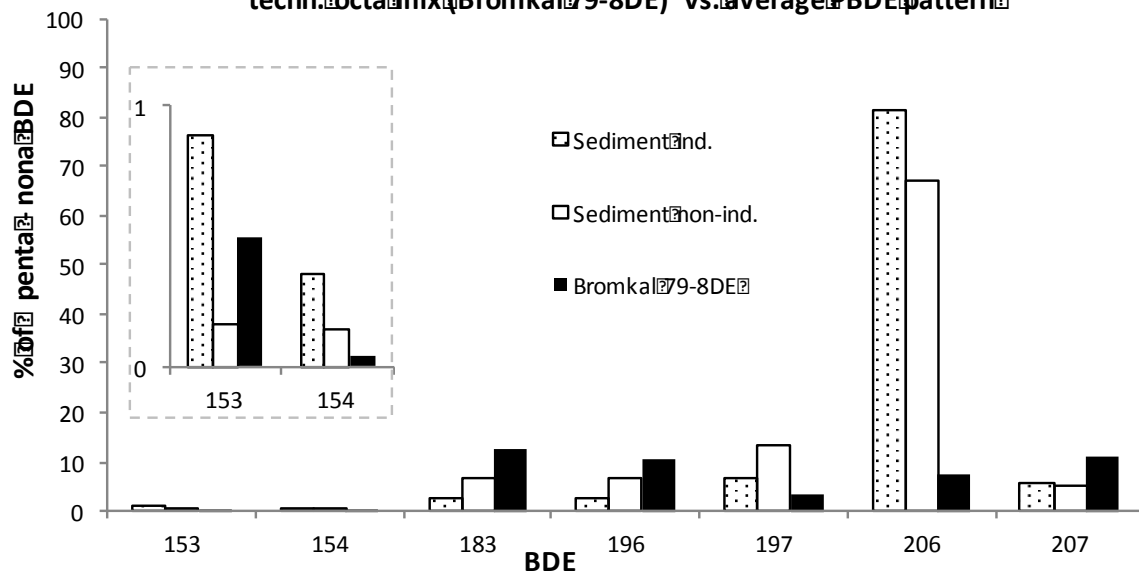
Figure 8 compares the average PBDE profile of the industrial area and the non-industrial one against the Penta-, Octa-, and Deca- technical PBDE mixes. While caution must be exercised when comparing congener profiles in environmental samples with those in the commercial formulations, as congener-specific differences in physicochemical properties will modify the congener profile between source and receptor; in general, no significant differences were observed between the pattern of PBDEs between the industrial and non-industrial area. Compared to the technical Penta-BDE mixture, the PBDE profile pattern in our sediment was shifted towards lower brominated congeners such as BDE-28, possibly indicating debromination. In the Penta-BDE mixture, the ratio of BDE-47:99 is 0.79⁵⁵, while in our samples a shift towards BDE-99 was observable, most likely due the stronger tendency of BDE-99 to partition to sediments, due to its higher K_{OW} and K_{OA} values⁵⁶. For the Octa-BDE technical mixture, the differences between our sample and the technical mixture most likely relate to infrequent application and emission of Octa-BDE in the UK, together with the presence of minor proportions of hexa- through nona-BDEs in the Deca-BDE formulation and/or environmental degradation of Deca-BDE congeners. Technical Deca-BDE on the other hand, showed little deviation from the pattern in our sediment, indicating widespread recent UK use and application of this technical mixture.

techn. penta mix (DE-71)¹ vs. Average PBDE pattern²



460

techn. Octa mix (Bromkal 79-8DE)¹ vs. Average PBDE pattern²



461

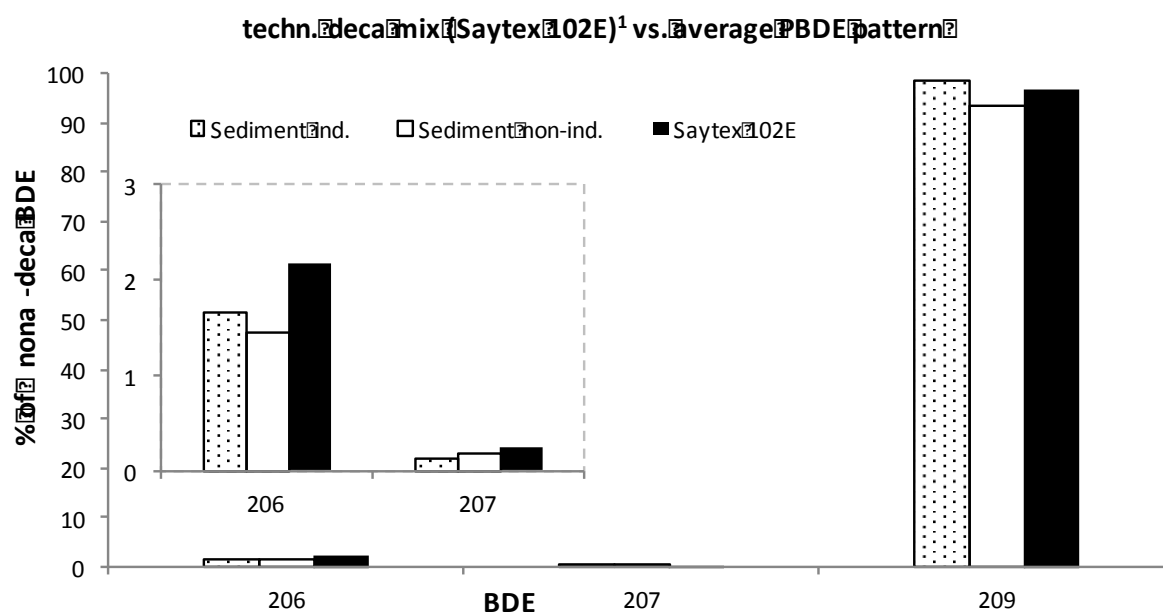


Figure 8. Comparison of an average PBDE profile in the industrial area (dotted) and outside the industrial area (white) to a technical penta / octa / deca BDE mix (black) – technical mixture values adapted from La Guardia et al.⁵⁵

3.7 Screening for degradation products and selected NBFRs

The UPLC-HRMS used in this study proved to be an excellent platform for the identification and quantification of PBDEs and NBFRs. Moreover, rapid HRMS analysis in full scan mode allows post-acquisition data analysis for further identification of compounds/transformation products of interest (e.g. potential degradation products and NBFRs). A limitation here is the possible degradation of acid-labile compounds as a result of the acid wash step in our extract clean-up procedure.

To screen for further brominated compounds in the sample set, a Br trace ($m/z = 78.918336 / 80.916290$) was queried from the full scan - all ion fragmentation (AIF) acquisition using Xcalibur software. This revealed the presence of brominated compounds with shorter retention times than brominated PBDEs. Further investigation of the accurate mass, isotope patterns and comparison to the high resolution mass spectrum of hydroxylated PBDE (OH-BDE) standards revealed the identified peaks as OH-BDEs (further details are provided in the

SI section). Unlike PBDEs, OH-BDEs have not been produced industrially and are not known by-products of technical brominated formulations^{57, 58}. However, OH-BDEs have been reported in biotic and abiotic samples of the aquatic and marine environment, such as salmon⁵⁷, mussels⁵⁹, algae⁶⁰ as well as sediments⁶¹, surface waters⁶² and sewage treatment plant effluents⁶³. Studies suggest that they are natural products of marine environments, as well as a result of metabolic biotransformation from anthropogenic PBDEs^{60, 62}. The position of the hydroxyl group (OH) has been postulated to be an indicator of whether OH-BDE congeners are formed through oxidation or metabolic reactions^{57, 59, 61}. Possible sources and transformation found in the literature include microbial aerobic degradation^{64, 65}, photochemical reactions of bromophenols⁶⁶ and PBDEs⁶⁷, transformation of bromophenols by marine bacteria⁶⁸ and a red algae enzyme⁵⁸, reactions of PBDEs with atmospheric OH radicals⁶², as well as in sewage treatment plants through oxidative reactions and excretion of human and animal metabolites⁶². Whether the OH-BDEs detected in the Thames sediments are of environmental and/or biological origin is beyond the scope of this paper. However, since OH-BDEs have been reported to exhibit similar or even enhanced toxic⁶⁹ and estrogenic⁷⁰ effects on both human⁷¹ and wildlife^{72, 73} compared to PBDEs, their presence and relevance needs to be further investigated.

Barber *et al.*¹⁹ reported on the presence of a wide range of NBFRs in UK sediments. However, screening of our sediment samples for those such as: 2,3,5,6-tetrabromo-*p*-xylene (TBX), tris(2,3-dibromopropyl) phosphate (TDBPP), tetrabromo-bisphenoldiallylether (TBBPA-DAE), tetrabromobisphenol-bis(2,3-dibromopropylether) (TBBPA-DBPE), octabromotrimethyl-phenylindane (OBTMPI/OBIND), pentabromophenol (PBP) and pentabromobenzyl acrylate (PBB-Acr) did not reveal them to be present in our study.

4 Summary

Brominated flame retardants have found wide application in consumer products and building materials. Densely populated areas such as London with its large industrial hinterland can thus act as emission sources of these chemicals. Since the river Thames passes through this area, it can act as an indicator of such emissions.

This is the first extensive study targeting several legacy BFRs and NBFRs in sediments along the tidal River Thames. Results indicate that BDE-209 is the predominant congener in all samples, accounting for ~ 95 % of total PBDEs detected, with a concentration range of <0.1 to 540 $\mu\text{g kg}^{-1}$ dw. This finding is of interest due to the recent listing of Deca-BDE under the Stockholm Convention, which underlines the current and future environmental concern over this BFR. Further, possible evidence of environmental debromination of Penta-BDE was observed through the elevated relative abundance of BDE-28 in sediment compared to that in the Penta-BDE formulation. NBFRs were detected in the following order (detection frequency): BEH-TEBP (76 %) > TBP (69 %) > BTBPE (51 %); with DBDPE (20 %), DP (11 %) and PBEB (7 %) identified only in a few samples. Concentrations of BEH-TEBP were found to be of a comparable range to those found for Σ_{12} BDEs in this study, as well as showing a similar concentration pattern along the river, possibly indicating a similar source input. Spatial variation analysis of the sediment samples further revealed that locations within the industrial area of London had significantly higher concentrations of Σ_{12} BDEs, HBCDDs, TBBPA, as well as BEH-TEBP, BTBPE and TBP. Analysis of HBCDD diastereomer patterns revealed samples from three locations within the industrial area possessed comparatively high concentrations and diastereomer profiles matching those of the technical mixture. This

could possibly indicate fresh input sources such as sewage treatment plants at these locations.

The presence of hydroxylated PBDEs suggests the presence of transformation products in our sediments. Sources, formation reactions and impact on the environment and human health of these compounds have to be further investigated, along with the presence of other possible transformation products.

5 Acknowledgements

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